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On the Reactions of Sodium Benzhydrol.

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

BY RAYMOND FOSS BACON.

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On the Reactions of Sodium Benzhydrol.

An exhaustive study by Nef[1] of benzhydrol and its derivatives, benzhydrol ether, bromdiphenyl methane, benzilic acid, etc., has shown that these substances possess very low dissociating-points. The dissociation-product common to all of them, diphenylmethylene, is not, however, capable of isolation as such. Similar results have been obtained by Miss Goldthwaite with the corresponding dibrom derivatives.[2] Since then it has been clearly proved by Nef[3] that all primary and secondary alcohols undergo analogous dissociation into water and alkylidenes, the sole difference being in the fact that the decomposition-point varies within considerable limits, 300° to 600°. We have, as yet, no accurate means for determining the exact percentage of water and ethylidene particles present, for instance, in alcohol or ether at the ordinary temperature. As ether decomposes at a temperature which is 50° lower than the decomposition-point of alcohol, 600°, ether must obviously contain more dissociated particles,

$$CH_3CH_2OCH_2CH_3 \rightleftarrows 2CH_3CH< + H_2O,$$

at the ordinary temperature than alcohol. This explains why ether burns slowly at ordinary temperatures, in the light, whereas this is not the case with alcohol, except in the presence of various catalytic agents, which have the effect of increasing most remarkably the percentage of the dissociated particles.

The experiments of Nef show further that if the hydroxyl hydrogen of an alcohol be replaced by a metal, such as Na, K, Ca, Ba, etc., the effect on the dissociating-point of the corresponding alcohol is most striking. The decomposition-point of sodium ethylate, for example, lies at 240°. Consequently there are, relatively, far more dissociated particles,

[1] Ann. Chem. (Liebig), **298**, 231-274.
[2] Am. Chem. J., **30**, 447.
[3] Ann. Chem. (Liebig), **318**, 138-230.

$$CH_3CH_2ONa \rightleftarrows CH_3CH< + H—ONa,$$

present at the ordinary temperature in sodium ethylate than in ether. Sodium ethylate, therefore, burns spontaneously, with considerable violence, in dry air or oxygen. The behavior of the metallic alcoholates of the aliphatic series has, in fact, been very thoroughly studied under the most varied conditions by Nef. He has found that they act as alkylating agents, and that they also decompose caustic alkalies with evolution of atomic hydrogen and can, therefore, act as reducing agents. Furthermore, it has been decisively established that the Geuther-Fröhlich reaction between carbonic oxide and sodium alcoholates is an alkylation phenomenon; *i. e.*, the reaction takes place in two stages, *viz.*, I.

$$CO + CH_3CH_2ONa \rightleftarrows CO + H—ONa + CH_3CH< \rightarrowtail$$

$$\rightarrowtail \begin{matrix} H \\ NaO \end{matrix}\!\!>\!CO + >CH—CH_3;$$

and then only to a slight extent according to II.

$$CH_3CH< + \begin{matrix} H \\ NaO \end{matrix}\!\!>\!CO \rightarrowtail \begin{matrix} CH_3CH_2 \\ NaO \end{matrix}\!\!>\!CO.$$

In these experiments, therefore, the yield of alkylated formic acid is usually exceedingly small. It was found in one instance to be very large, namely, with 1,3-decyl alcohol.[1] On the other hand, the yield in the case of the alkylation of acetic acid with sodium alcoholates was invariably large—15 to 30 per cent. As the alkylidene can also necessarily interact with the caustic alkali—the other dissociation-product—with evolution of hydrogen and the formation of an aldehyde, ketone, or fatty acid, it is obvious that alkylation by means of sodium alcoholates can never take place quantitatively.[2]

A study of the salts of the aromatic alcohols, such as benzyl alcohol and benzhydrol, from the point of view developed by the work of Nef seemed especially desirable, and, consequently,

[1] Cf. Nef: Ann. Chem. (Liebig), **318**, 150; Beatty: Am. Chem. J., **30**, 224.
[2] Ann. Chem. (Liebig), **318**, 148.

work in this direction has been undertaken in this laboratory at Dr. Nef's suggestion, and under his guidance, by Mr. Higley and myself. I have confined my experiments chiefly to the benzhydrol series. As Mr. Higley's results in the benzyl series will presumably not be published for some time,[1] I shall at times refer briefly to them where they have a bearing on my own work. A study of the dissociation phenomena in the benzhydrol series seemed of interest first, because Knoevenagel[2] has recently, without sufficient basis, assumed a direct dissociation of benzhydrol into hydrogen and benzophenone, and secondly because it would be possible here to trace quantitatively all the reaction-products with great ease, as they must be crystalline, and their quantitative separation has already been worked out thoroughly by Nef (*loc. cit.*). The experiments performed with sodium benzhydrol were found to be entirely in harmony with the data obtained by Nef. It was possible to alkylate formic, acetic, and isobutyric acids by means of this salt. In the case of the acetic acid a 75 per cent yield of the monoalkylated acetic acid was actually obtained. These experiments finally led to an investigation of the action of sodium on benzyl acetate and allied compounds, and thus to a complete revision of the work Conrad and Hodgkinson[3] carried out in this direction some twenty-five years ago.

Preparation of Sodium Benzhydrol.—The benzhydrol used in all of my experiments was prepared according to the directions of Nef.[4] It was dissolved in 5 volumes of absolute ether, containing the calculated amount of sodium in the form of wire; the mixture was then heated under a reversed condenser until the metal had all disappeared. On cooling, sodium benzhydrol often crystallized out in large, transparent, colorless, crystalline plates, 2 to 3 cm. in length.

1.3830 grams substance, treated with water, required 65.1 cc. N/10 H_2SO_4 for neutralization.

1.0930 grams substance, treated with water, required 52.1 cc. N/10 H_2SO_4 for neutralization.

[1] Am. Chem. J., **30**, 225, foot-note.
[2] Ber. d. chem. Ges., **36**, 588.
[3] Ann. Chem. (Liebig), **193**, 298; **201**, 166.
[4] *Ibid.*, **298**, 231–233.

	Calculated for $(C_6H_5)_2CHONa$.	Found.	
Na	11.1	10.8	10.9

The salt quickly gains in weight in the air, owing to rapid absorption of water and oxygen ; it turns green or greenish-blue in the light, and becomes colorless again over night. This phenomenon was noted for seven successive days, and reminds one of the behavior of benzhydrol ethyl ether described by Linnemann,[1] although I have never noticed these phenomena in the latter case.

Dissociation of Sodium Benzhydrol.—The decomposition-point of this substance lies about 50° below that of benzhydrol, namely, at 250°. The salt, consequently, burns with considerable speed in dry air at the ordinary temperature. The products formed by heating the salt to the dissociating-point are benzene, sodium benzoate, and diphenyl methane, including, at times, also some tetraphenyl ethane and ethylene. Three experiments were carried out quantitatively under slightly different conditions.

1. Twenty grams of sodium benzhydrol were heated in a distilling-flask for eight and a half hours in a metal bath, at a temperature ranging from 240° to 270°. The distilling-flask was connected with a condenser, a receiver, and an azotometer. The salt became at first bluish in color, but at the end was colorless again. No gaseous products were formed ; the receiver contained 3.4 grams of liquid, from which, on fractionation, 2.9 grams of benzene, boiling from 75° to 80°, were obtained. The residue in the distilling-flask was worked up for neutral and acid products by extracting with dilute sodium hydroxide and ether. The ether extract gave, on crystallization from ligroin, 6.2 grams of benzhydrol, melting at 69°, and the filtrate gave 2.5 grams of diphenyl methane. Four and five-tenths grams of benzoic acid were obtained from the alkaline solution.

2. A second experiment, similar to 1, and using the same amount of material, but heating during four hours at 260° to 290°, and for a short time to 300°, showed some blackening

[1] Ann. Chem. (Liebig), **133**, 6.

and gas evolution (only at 300°). The reaction-products were found to be 3.1 grams of benzene, 4.2 grams of benzoic acid, 7.7 grams of diphenyl methane, 0.5 gram of tetraphenylethylene, 0.4 gram of tetraphenyl ethane, and 1.1 grams of benzhydrol.

Benzophenone was not present in either 1 or 2, as was proved by digestion of the neutral product with alcoholic phenylhydrazine, after removal of the benzhydrol with cold ligroin.

3. Twenty grams of sodium benzhydrol were heated in a sealed tube at 270° to 280° for forty hours (five successive days of eight hours each). No pressure was observed on opening the tube. The residue had a yellowish tinge, and was somewhat blackened in the middle. The reaction-products were determined as 2.6 grams of benzene, 5.5 grams of benzoic acid, 7.3 grams of diphenyl methane, and 3.1 grams of benzhydrol. Therefore, the following main reaction takes place on heating sodium benzhydrol to its decomposition-point:

$$2(C_6H_5)_2CHONa \rightarrowtail 2(C_6H_5)_2C< + 2H{-}ONa \rightarrowtail$$
$$(C_6H_5)_2C(ONa)_2 + 2H + (C_6H_5)_2C< \rightarrowtail$$
$$(C_6H_5)_2C=O + Na_2O + H_2C(C_6H_5)_2.$$

The reaction is obviously entirely analogous to the one which takes place between benzaldehyde and potassium hydroxide at the ordinary temperature.[1] That under the conditions of the experiment the benzophenone first formed must be rapidly and completely converted into equal amounts of benzene and sodium benzoate,

$$(C_6H_5)_2C{=}O + NaOH \rightarrowtail C_6H_5COONa + H.C_6H_5,$$

follows from the observations of Chancel[2] on benzophenone, and was also established by special experiment.

An intimate mixture of 10 grams of benzophenone and 2.2 grams of sodium hydroxide were heated for one hour at 260° to 270° (apparatus as in 1, above); 3.6 grams of benzene, boiling from 78° to 80°, were obtained from the distillate in the

[1] Nef: Ann. Chem. (Liebig), **298**, 301–302.
[2] *Ibid.*, **72**, 280.

receiver ; the residue in the distilling-flask gave 4.5 grams of benzoic acid.

The small amount of tetraphenylethylene and ethane observed in Experiment 2, above, is probably due to a polymerization of the nascent molecules of diphenyl methylene,

$$(C_6H_5)_2C<,$$

and diphenyl methyl,

$$(C_6H_5)_2CH—.$$

The Spontaneous Combustion of Sodium Benzhydrol in Dry Air.—According to Nef's interpretation of combustion phenomena,[1] the following reaction between the dissociated sodium benzhydrol molecules and the active oxygen molecules of the air must take place at considerable speed on passing dry air and oxygen over sodium benzhydrol at the ordinary temperature :

$$(C_6H_5)_2C< + 2NaOH + \overset{|}{O}—\overset{|}{O} \rightarrowtail (C_6H_5)_2C(ONa)_2 + H_2O_2 \rightarrowtail (C_6H_5)_2CO + Na_2O_2 + H_2O.$$

This was found to be the case. The sodium peroxide is, however, in great part used up in oxidizing the unchanged diphenylmethylene particles,

$$(C_6H_5)_2C< + Na_2O_2 \rightarrowtail (C_6H_5)_2C=O + Na_2O,$$

so that only 21.67 per cent of the sodium peroxide was actually isolated, as such, at the end of the experiment. No trace of peroxide, $(C_6H_5)_2C\begin{cases}O\\|\\O\end{cases}$, such as would be demanded by Engler and Bach's interpretation of combustion phenomena,

$$NaOH + (C_6H_5)_2C< + \overset{|}{O}—\overset{|}{O} \rightarrowtail (C_6H_5)C\begin{cases}O\\|\\O\end{cases} + NaOH,$$

was found in my oxidation experiments. Nef also failed to obtain a trace of the stable acetone peroxide of Baeyer in his experiments on the oxidation of sodium isopropylate.[2]

[1] Ann. Chem. (Liebig), **298**, 294–301, 322–332; **318**, 177–182.

[2] *Ibid*, **318**, 181.

1. Twenty-five grams of sodium benzhydrol were placed in a large flask and a stream of air, dried by a combustion train, was slowly passed over it. A perceptible rise of temperature was observed after an hour and the gain in weight, after nine hours, was 1 gram. The mass had now a greenish tint and appeared moist. Dry oxygen was then passed over the mixture for ten hours, with no apparent change. The mass was directly extracted with absolute ether; no benzene was present, and the ether extract gave, on fractionation under 25 mm., 16.2 grams of perfectly pure benzophenone boiling at 180° to 182°. It solidified immediately on addition of a crystal of benzophenone, and then all melted at 47°. A portion, 5 grams, gave, on digestion with 3.7 grams of phenylhydrazine and an equal weight of alcohol, 7 grams of benzophenone phenylhydrazone melting at 137° (theory 7.47 grams). The portion insoluble in ether, 7 grams, was treated with water and extracted with ether. The alkaline solution gave a marked test for carbonic acid, and, on acidifying, 0.8 gram of benzoic acid, melting at 121°, was obtained. The solution also gave a most pronounced test for hydrogen peroxide with bichromate and ether. On treatment of a portion of the solution with benzoyl chloride, according to v. Pechmann,[1] a precipitate of dibenzoyl peroxide, melting at 104°, was obtained.

2. In order to determine the amount of hydrogen peroxide quantitatively, a fresh oxidation experiment was carried out with 10 grams of sodium benzhydrol. During the oxidation (air eight hours, oxygen forty-four hours) the distilling-flask containing the salt was kept immersed in ice-water. The reaction-products were at once treated with water and an excess of potassium iodide added. The amount of iodine set free was then determined by means of sodium thiosulphate (preliminary experiments having shown that this method was accurate for the work in hand); 0.39 gram of sodium peroxide, or 21.67 per cent of the amount demanded by the above theory, was found.

On the Combustion or Oxidation of Bromdiphenylmethane.— The experiments of Nef have proved that not only primary

[1] Ber. d. chem. Ges., **27**, 1511.

and secondary alcohols, their salts, and ethers, but also the primary and secondary alkyl haloids, the aldehydes, ketones, fatty acids, substituted ammonias, paraffines, etc., undergo methylene dissociation. Ethane, toluene, diphenyl methane, when first oxidized, give acetaldehyde, benzaldehyde and benzophenone, respectively, because these substances are partially dissociated at the ordinary temperature, *e. g.*,

$$CH_3CH_3 \rightleftarrows CH_3CH< + H_2.$$

It was, therefore, of interest to try the action of oxidizing agents on bromdiphenyl methane. This substance possesses, as Nef has shown, a low dissociation-point, 250°. It ought, therefore, to oxidize slowly in dry air, at the ordinary temperature, to benzophenone. Miss Goldthwaite has, indeed, shown that such an oxidation takes place with the analogous paradibromdiphenyl methyl bromide. When, however, either of these compounds is heated to the decomposition-point, 250°, without air access, hydrogen bromide is eliminated quantitatively, but the diphenyl methylene residues first set free either polymerize directly to the dimolecular derivatives, or give these end-products by an intermediate alkylation and subsequent loss of hydrogen bromide,

$$(C_6H_5)_2C< + HCBr(C_6H_5)_2 \rightarrow (C_6H_5)_2CH—CBr(C_6H_5)_2.$$

That the dissociation of these compounds is monomolecular and not bimolecular is furthermore proved by the fact that, when the heating is carried out in a stream of dry air or oxygen, benzophenone and paradibrombenzophenone, respectively, are formed quantitatively. This proves that the diphenymethylene residues first set free combine preferably with the oxygen to give the corresponding oxides. The reaction is, therefore, perfectly analogous to the combustion of sodium benzhydrol presented above. In the light of what has just been said, the results of the following experiments with bromdiphenyl methane are self-evident :

1. Ten grams of bromdiphenyl methane were treated in the cold, and in a solution acidified with sulphuric acid, with aqueous potassium permanganate until no further decoloriza-

tion took place. The solution was extracted with ether and the oil obtained was then digested with phenylhydrazine and alcohol. Nine and one-tenths grams of benzophenone phenylhydrazone, melting at 136°, were obtained.

2. Five grams of bromdiphenylmethane were placed in a distilling-flask connected with a reversed condenser and dry oxygen steadily passed through the molten substance, which was heated in a metal-bath at 160° to 170°. Streams of hydrogen bromide came off at first, and practically ceased after three and one half hours' heating. The oil left in the distilling-flask boiled chiefly at 160° to 170° under 10 mm. pressure, and gave, on digestion with phenylhydrazine and alcohol, 5.3 grams of benzophenone phenyl hydrazone melting at 137°. Nine-tenths gram of the tetraphenyl ethylene, melting at 218°, were found in the distilling-flask after the removal of the benzophenone by distillation.

3. Five grams of bromdiphenyl methane, dissolved in absolute ether, were left standing in the cold for two weeks with 3 grams of sodium in the form of wire. One and two-tenths grams of tetraphenyl ethane and 1.1 grams of diphenyl methane were obtained as reaction-products.

The Action of Sodium Benzhydrol on Benzhydrol Acetate.—As is well known through the work of Geuther, Claisen and others, esters of acetic acid are converted into acetoacetic ether by treatment with sodium or sodium alcoholates. The reaction has been shown by Nef to belong to the category of olefine condensations, and is therefore reversible. In connection with the earlier experiments on the esters of acetic acid, it was found that esters containing an aliphatic group, such as methyl, propyl, and isoamyl acetate, all give a fair yield of the corresponding acetoacetic ester, on treatment with sodium or with sodium alcoholates. On trying the experiment with benzyl acetate and sodium, however, Conrad and Hodgkinson found, to their great surprise, that no trace of acetoacetic benzyl ester was obtained.[1] An interaction between the reagents took place at 135° and then pro-

[1] Ann. Chem. (Liebig), **193**, 298.

ceeded with some violence. According to their investigations, benzyl hydrocinnamate,

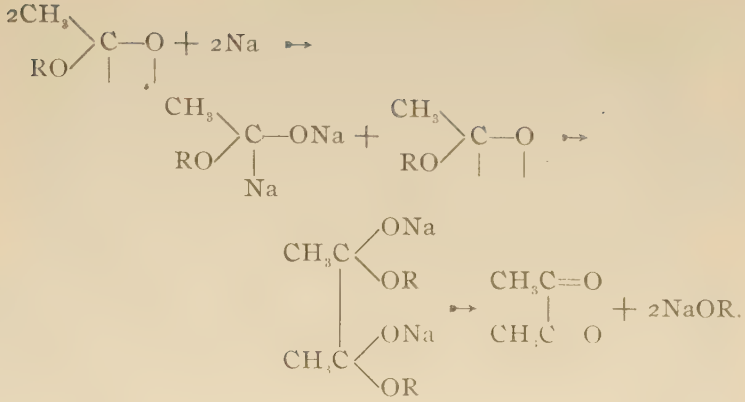
$$C_6H_5CH_2CH_2COOCH_2C_6H_5,$$

is the chief reaction-product. Such a result could now be readily understood in view of the experiments of Nef on the alkylation of the fatty acids by means of sodium alcoholates. The phenyl methylene particles, resulting from the dissociation of the sodium benzylate first formed, must alkylate the unchanged benzyl acetate as follows :[2]

$$C_6H_5CH< + H{-}CH_2COOCH_2C_6H_5 \rightarrowtail C_6H_5CH_2CH_2COOCH_2C_6H_5.$$

A more careful investigation of the reaction of Conrad and Hodgkinson, which is described in detail below, has proved that much benzyl ether is formed besides benzyl hydrocinnamate. The question now arises, why do not benzyl acetate and sodium interact to give an ester of acetoacetic acid ? The same question presents itself in the case of benzhydrol acetate. The problem was first taken up in this laboratory by Shaklee, who proved that benzyl acetate and benzhydrol acetate readily react with sodium in absolute ethereal solution in the cold. He found that very little hydrogen was given off in the course of the reaction, and that the chief products were acetic acid, and benzyl alcohol, or benzhydrol, respectively. In both cases, however, the formation of a small amount of diacetyl was observed. Shaklee established this rigidly by the isolation of the osazone, which was analyzed and found to be identical in its properties with the statements given in the literature. This result, in conjunction with the other facts observed, proves that some esters of acetic acid can react with sodium in a manner entirely different from ethyl acetate. The experiments of Nef on the action of sodium on carbonyl compounds[1] make it exceedingly probable that the following reaction between sodium and acid esters can take place :

[1] Ann. Chem. (Liebig), **318**, 144 ; Cf. Am. Chem. J., **30**, 225, foot-note.
[2] Ann. Chem. (Liebig), **308**, 283, 292 ; Cf. Acree : Am. Chem. J., **29**, 588.



No hydrogen is formed in this reaction and the yield of diacetyl must necessarily remain low, because all orthodicarbonyl compounds undergo a benzilic acid rearrangement, *i. e.*, a conversion into glycollic acid derivatives, especially in the presence of strong alkali. It is, therefore, quite probable that dimethylglycollic acid was formed in Shaklee's experiments but was overlooked by him.

The fact that ethyl isobutyrate gives diisopropylglycollic acid derivatives as the chief reaction-products[1] on treatment with sodium, in absolute ethereal solution, taken in connection with Shaklee's isolation of diacetyl, makes this assumption almost a certainty. These results at once bring up the question whether ethyl acetate itself may, to some extent, not react in an analogous manner with metallic sodium. The amount of hydrogen actually evolved in the manufacture of acetoacetic ether from acetic ether and sodium is only 36.5 per cent of the theoretical amount in the most favorable case.[2] The preliminary experiments which I have carried out in this direction are very striking, and seem to justify these conclusions. When ethyl acetate, carefully dried, is diluted with 10 parts of absolute ether and treated with one atomic proportion of sodium, the metal disappeared entirely after twenty-four hours' standing. Only traces of acetoacetic ether and of hydrogen were obtained un-

[1] Hantzsch: Ber. d. chem. Ges., **20**, 2332; Ann. Chem. (Liebig), **249**, 54; **246**, 129.
[2] Cf. Meyer: J. prakt. Chem., [2], **65**, 528.

der these conditions, although the experiment was tried five times, using 176 grams of ethyl acetate in each experiment. It is the intention of Dr. Nef to investigate this reaction in the near future with the greatest of care. The results obtained show, however, that the recent assumption of Michael[1] that ethyl acetate first gives the salt $CH_2NaCOOC_2H_5$, etc., on treatment with sodium cannot possibly be correct. Experiments in this connection by Higley have further proved that a mixture of 2 molecules of ethyl acetate and 1 molecule of sodium ethylate, on standing for a week at ordinary temperatures, gives a 26.7 per cent yield of acetoacetic ester; on standing for twenty-five days a 36.1 per cent yield of the ester was obtained.[2]

In order to determine why the corresponding condensation between sodium benzylate and benzyl acetate, as well as between sodium benzhydrol and benzhydrol acetate does not take place to any extent, it was obviously first necessary to prepare benzyl- and benzhydrolacetoacetate and study their properties.

Benzyl Acetoacetate, $CH_3COH : CHCOOCH_2C_6H_5$.—This ester has been prepared and analyzed by Shaklee, who obtained it, almost quantitatively, by heating a mixture of 20 grams of benzyl alcohol and 40 grams of acetoacetic ethyl ester in a distilling-flask connected with a condenser and Brühl apparatus. The bath was kept at 160° and as soon as no more ethyl alcohol distilled over, the apparatus was exhausted. Thirty-four grams of benzyl acetoacetate, boiling at 162° to 164° under 16 mm. pressure, was obtained as a colorless mobile oil, smelling like ordinary acetoacetic ester. The oil boils, with some decomposition, at about 270°, gives a blood-red coloration with alcoholic ferric chloride, is insoluble in alkali carbonates, but dissolves without decomposition in cold aqueous sodium hydroxide.

The copper salt, which has been analyzed by Higley, is precipitated quantitatively by means of aqueous alcoholic copper acetate. It crystallizes well from benzene, and melts at 156°. Experiments by Shaklee and Higley have shown that benzyl-

[1] Ber. d. chem. Ges., **33**, 3731.

[2] Cf. E. V. Meyer: J. prakt. Chem., [2], **65**, 528.

acetoacetate is never formed in amounts greater than 2 per cent on treatment of benzyl acetate with sodium or with sodium benzylate under the most varying conditions (20°, 100°, 140°). Higlee's experiments prove, furthermore, that benzyl acetoacetate is readily decomposed by heating it with sodium benzylate at 100° or at a still higher temperature. Consequently only traces of benzyl acetoacetate are obtained from mixtures of benzyl acetate and sodium or sodium benzylate when heated above 100°. These data, therefore, prove that benzyl acetoacetate is formed from its components by the aldol condensation, but in relatively far smaller amounts than ethylacetoacetate. The great difference in the yield, as the reaction is reversible, is simply due to the far greater relative instability of benzyl acetoacetate My own experiments in the benzhydrol series confirm in every way these observations of Higley.

Benzhydrol Acetoacetate, $CH_3COH : CHCOOCH(C_6H_5)_2$.—Fifty grams of benzhydrol dissolve in 100 grams of ordinary acetoacetic ether with marked lowering of temperature (23° to 10°). This mixture was heated in an oil-bath at 150° for one hour; much ethyl alcohol distilled over. The oil left in the distilling-flask was now heated *in vacuo* at 200°, the non-volatile portion dissolved in cold sodium hydroxide, and the neutral constituents extracted with ether. The alkaline solution gave, on acidifying with sulphuric acid and extracting with ether, 51 grams of crude oil, which soon solidified. By crystallizing from ether-ligroin, benzhydrol acetoacetate was obtained in colorless plates, melting at 56°. The substance is very soluble in the ordinary organic solvents except ligroin. It smells like acetoacetic ether and gives a deep purple coloration with ferric chloride. It is insoluble in alkali carbonates and, like all benzhydrol derivatives, gives a deep red coloration with concentrated sulphuric acid.

0.2291 gram substance gave 0.6329 gram CO_2 and 0.1228 gram H_2O.

	Calculated for $CH_3COH : CHCOOCH(C_6H_5)_2$.	Found.
C	76.1	75.4
H	6.0	6.0

The copper salt is precipitated quantitatively by means of aqueous alcoholic copper acetate. It crystallizes from benzene as a powder, melting at 174° to 176°. The following experiments show that, at best, it is possible to obtain benzhydrol acetoacetate only in very small amounts from mixtures of benzhydrol acetate and sodium benzhydrol; this is due, in part or entirely, to the great instability of sodium benzhydrol acetoacetate under these conditions. It may, however, also be due in part to the greater stability of the orthoacetic acid addition-product, $CH_3C(OCH(C_6H_5)_2)_2ONa$, which must necessarily be first formed on mixing these reagents.[1]

1. Twenty-two and six-tenths grams of benzhydrol acetate (2 mols.) and 10.3 grams of sodium benzhydrol were intimately mixed. There is a noticeable heat evolution, owing to the formation of the ortho addition-product. The mixture was heated in a sealed tube at 100° for fifteen hours. The mass was then treated with dilute sulphuric acid and worked up as usual for products soluble in sodium hydroxide and sodium carbonate. A small amount of β-diphenylpropionic acid, the monoalkylated acetic acid (see below), was obtained, besides acetic acid. The sodium hydroxide solution gave 0.4 gram of benzhydrol acetoacetate, melting at 53°, and identical in its properties with the ester described above. The neutral portion gave 14 grams of benzhydrol, which melted at 68° and crystallized from ligroin. Ten grams of oil, boiling at 176° to 183° under 17 mm. pressure, were also obtained. This was proved to be free from benzophenone by digestion with alcoholic phenylhydrazine. On saponification with alcoholic potash the oil gave 7.8 grams of benzhydrol, hence it consisted of benzhydrol acetate.

2. Five grams of benzhydrol acetoacetate and 8 grams of sodium benzhydrol (2 mols.), treated as in 1, gave 6 grams of benzhydrol and small amounts of benzophenone; the latter was probably formed through a spontaneous oxidation of

[1] Claisen: Ber. d. chem. Ges., **20**, 648.

sodium benzhydrol, as the mixture stood in the air before being worked up. No unchanged benzhydrol acetoacetate was found.

3. Twenty-two and six-tenths grams benzhydrol acetate (4 mols.) and 5.1 grams of sodium benzhydrol, treated as in 1, gave only traces of β-diphenylpropionic acid, 8.5 grams of benzhydrol, and 14.7 grams of unchanged benzhydrol acetate.

4. Ten grams of benzhydrol acetate, dissolved in absolute ether and treated with 7 grams of sodium in the form of wire, reacted completely in the cold. On working up as in 1, 4 grams of benzhydrol and only traces of benzhydrol acetoacetate were obtained. It is to be emphasized that Shaklee obtained also small amounts of diacetyl under similar conditions.

The experiments, 1 to 4, show that mixtures of benzhydrol acetate and sodium benzhydrol or sodium do not interact to give an appreciable amount of benzhydrol acetoacetate. It was now of interest to determine what would happen if molecular amounts of these reagents were heated to a higher temperature (150° to 300°). It is obvious from the experiments of Nef that the dissociated molecules coming first from the sodium benzhydrol, and also from the dissociated benzhydrol acetate (see below), might alkylate the benzhydrol acetate or the sodium acetate,

$$(C_6H_5)_2C< + H—CH_2COOM \rightarrow (C_6H_5)_2CHCH_2COOM,$$

which would result in the formation of β-diphenylpropionate or its benzhydrol ester. The experiment was therefore tried and, under the most favorable conditions (300°), a yield of 75 per cent of the theoretical amount of β-diphenylpropionic acid was actually obtained.

Benzhydrol β-Diphenylpropionate, $(C_6H_5)_2CHCH_2COOCH(C_6H_5)_2$. — As this ester might be formed by direct alkylation of benzhydrol acetate it was synthesized and studied. On account of the very stable properties ascribed by Conrad and Hodgkinson (*loc. cit.*) to the analogous benzyl hydrocinnamate, it was at first expected that the ester must be exceedingly difficult to saponify. This was

found, however, not to be the case, and later experiments (see below) with the real synthetic benzyl hydrocinnamate have proved that it also can be saponified with the greatest of ease by means of alcoholic potassium hydroxide in the cold.

β-Diphenylpropionic acid was prepared according to the directions of Henderson.[1] The melting-point of the acid, after crystallization from ligroin, was found to be 155°, whereas Henderson gives 151°. The acid crystallizes in needles and gives no coloration on standing with concentrated sulphuric acid. It is not volatile with steam. Heated with an equal weight of sodium benzhydrol for six hours, in a sealed tube, at 300° to 310°, it was recovered entirely unchanged. The potassium salt of β-diphenylpropionic acid, dissolved in an equal weight of the free acid, was now heated with the theoretical amount of bromdiphenylmethane for five hours at 150° to 160°. The neutral product thus obtained, which was insoluble in cold ether and soluble in cold benzene, was recrystallized from alcohol and colorless needles, melting at 112°, were obtained. The ester is difficultly soluble in ether and cold alcohol, but very soluble in benzene.

0.1831 gram substance gave 0.5747 gram CO_2 and 0.1072 gram H_2O.

	Calculated for $(C_6H_5)_2CHCH_2COOCH(C_6H_5)_2$.	Found.
C	85.7	85.4
H	6.1	6.2

Benzhydrol β-diphenylpropionate was saponified with the greatest ease by heating 5 grams in an oil-bath at 110°, for one hour, with 1.25 mol. potassium hydroxide in 10 grams alcohol. Two grams of benzhydrol and 2.5 grams of β-diphenylpropionic acid (theory 2.8 grams), melting at 154°, were obtained as reaction-products.

On the Alkylation of Acetic Acid by Sodium Benzhydrol.— This was accomplished in a variety of ways, all of which depend on the same principle, namely, the absorption of an acetate by diphenylmethylene coming from the dissociation of a

[1] J. Chem. Soc. (London), **59**, 734.

benzhydrol salt. The following experiments need, therefore, no further elucidation :

1. Ten grams of ethyl acetanilide and 12 grams of sodium benzhydrol were carefully mixed in a sealed tube until homogeneous, and were then heated for eight hours at 160° to 170°, and finally for three hours at 220°. The reaction-products were found to be as follows : 6.5 grams of ethyl aniline, 6.1 grams of benzhydrol, 1.1 grams of benzhydrol ether, traces of tetraphenyl ethane, and a small amount of benzophenone (identified as phenylhydrazone, 1.7 grams melting at 136°, being obtained). The solid acid product was found to consist only of β-diphenylpropionic acid (1.1 grams melting at 155°).

2. A second experiment, using 10 grams of ethyl acetanilide and 15 grams sodium benzhydrol, gave, after heating in a sealed tube for fifty hours (in periods of about eight hours daily), 6.5 grams of ethyl aniline, 5.2 grams benzhydrol, 1.5 grams of β-diphenylpropionic acid, 1.4 grams of tetraphenylethane, and a small amount of benzophenone (1.2 grams of phenylhydrazone being isolated).

3. 25 grams of benzhydrol acetate and 7 grams of quicklime were intimately mixed and heated in a sealed tube for six hours at 230° to 250°. Four-tenths gram of β-diphenylpropionic acid, 7.5 grams of tetraphenylethane, 6 grams of benzhydrol ether, 3.2 grams of benzhydrol, besides a small amount of benzophenone (4.1 grams phenylhydrazone) were obtained as reaction-products.

This experiment is of interest in connection with the formation of *n*-butyric acid, observed by Ljubawin,[1] on heating ethyl acetate with quicklime at 250° to 280°. Calcium ethylate and acetate are obviously first formed,

$$2CH_3COOCH_2CH_3 + 2CaO \rightarrowtail Ca(OCOCH_3)_2 + Ca(OCH_2CH_3)_2$$

the ethylidene, resulting from the dissociation of calcium ethylate, alkylates the acetate, giving calcium butyrate.

4. An intimate mixture of 16 grams benzhydrol acetate and 20 grams of sodium benzhydrol was heated for thirty hours, in

[1] Jour. Russ. Chem. Ges., **12**, 81.

a sealed tube, at 150° to 160°. There was no pressure on opening the tube, and 1.5 grams β-diphenylpropionic acid, besides 3.1 grams of benzhydrol β-diphenylpropionate were obtained. The other products were 19 grams benzhydrol, 1.5 grams benzhydrol ether, 1 gram tetraphenylethylene, traces of tetraphenylethane and a small amount of benzophenone.

5. Twelve grams of benzhydrol acetate and one atomic proportion of sodium (1.2 grams) were heated under a reversed condenser. There was no action at 100°; as soon as the bath reached 130° to 140° the metal dissolved rapidly and, after an hour's heating at that temperature, the following products were obtained: 1.1 grams β-diphenylpropionic acid, 6.5 grams of benzhydrol, 0.5 gram tetraphenylethylene, besides traces of the corresponding ethane derivative, and benzophenone (3.1 grams phenylhydrazone).

It will be noticed that the yield of monoalkylated acetic acid obtained in experiments 1 to 5 is not very large. At first this was attributed to a decomposition of this acid because Nef has shown that the fatty acids have comparatively low dissociation points.[1] Furthermore, the fact observed by Karsten[2] that β-diphenylpropionic acid gives benzophenone by oxidation with potassium permanganate points to a possible dissociation of the acid into diphenylmethylene and acetic acid. On further study, however, β-diphenylpropionic acid was found to be an exceedingly stable substance, with a decomposition-point certainly above 400°. The following experiment with benzhydrol acetate and sodium benzhydrol proves finally that the yield of monoalkylated acetic acid can be increased to 75 per cent of the theoretical amount by simply heating higher, namely, to 300°.

Ten grams benzhydrol acetate and 20 grams of sodium benzhydrol were mixed as thoroughly as possible in a sealed tube and then heated to 300° to 310° for six hours. The temperature accidentally ran up to 350° for a very short time. The result was 7.5 grams β-diphenylpropionic acid, 0.2 gram ben-

[1] Ann. Chem. (Liebig), **318**, 220.
[2] Ber. d. chem. Ges., **26**, 1579.

zoic acid, 4 grams diphenylmethane, and benzophenone (6.5 grams phenylhydrazone).

It should be emphasized at this point that, aside from the formation of β-diphenylpropionic acid by direct alkylation, with or without the intermediate formation of an acetoacetic acid derivative, another possible interpretation presents itself and was carefully considered. The benzophenone first formed by the decomposition of the sodium benzhydrol (see above),

$$(C_6H_5)_2C< + 2HONa \rightarrowtail (C_6H_5)_2C{=}O + Na_2O + 2H,$$

might act as such with the benzhydrol acetate by addition, thus:

$$(C_6H_5)_2C{-}O + HCH_2COOCH(C_6H_5)_2 \rightarrowtail$$

$$(C_6H_5)_2C\begin{cases} CH_2{-}COOCH(C_6H_5)_2 \\ OH \end{cases},$$

the resulting β-oxydiphenylpropionate must then lose water and take up 2 atoms of hydrogen to give β-diphenylpropionic acid. This interpretation is *à priori* highly improbable, for a variety of reasons, which need hardly be discussed in detail here. Suffice it to state that I made many attempts to condense benzophenone with salts of acetic and isobutyric acids, but without positive results. Furthermore, the following experiments were carried out in order to ascertain whether the yield of alkylated fatty acid is increased by an addition of benzophenone :

1. An intimate mixture of 10 grams of benzhydrol acetate, 10 grams of sodium benzhydrol and 5 grams benzophenone was heated in a sealed tube for six hours at 300°. Three and nine-tenths grams of β-diphenylpropionic acid, 3.5 grams diphenylmethane, 3.8 grams of benzhydrol and benzophenone (9 grams of phenylhydrazone) were obtained.

2. An intimate mixture of 10 grams benzhydrol acetate and 10 grams of sodium benzhydrol was heated in a sealed tube at the same time and in the same furnace as used in 1. The products formed were 3.4 grams β-diphenylpropionic acid, 3.4

grams benzhydrol, 4 grams diphenylmethane, and benzophenone (4.5 grams phenylhydrazone).

These experiments show very clearly that a considerable portion of the sodium benzhydrol decomposes as such (see above),

$$2(C_6H_5)_2CHONa \rightarrow (C_6H_5)_2C{=}O + Na_2O + (C_6H_5)_2CH_2,$$

giving benzophenone and diphenylmethane, and these are found mostly unchanged at the end of the experiment. This explains why it is necessary to use more than 1 molecular proportion of sodium benzhydrol in order to obtain a very large yield of β-diphenylpropionic acid (see above experiment with 2 molecular proportions of alcoholate at 300° to 310°). The slightly larger yield of monoalkylated acetic acid obtained in experiment 1, as compared with experiment 2, is easily understood because a portion of the benzophenone added must necessarily be reduced to benzhydrol[1] by the atomic hydrogen set free by the action of diphenylmethylene on sodium hydroxide. For that reason also the amount of diphenylmethane obtained in 1 is proportionally less than that found in 2.

The reactions under consideration therefore unquestionably belong to the category of alkylation phenomena. That the acetyl radical is alkylated directly by the diphenylmethylene particles, and not indirectly through an intermediate acetoacetic ether formation, is in the highest degree probable from the data presented above on the benzyl and benzhydrol acetoacetate.

There are, however, undoubtedly some cases where the alkylation depends partially or entirely on an intermediate formation of acetoacetic acid derivatives, and other cases where it is impossible to decide decisively between these two possibilities—which necessarily, however, lead to the same end result.

Furthermore, there is no doubt that the hydrogen atom in formic acid derivatives, X—C$\overset{O}{\underset{H}{<}}$, and the tertiary hydrogen

[1] Cf. Nef: Ann. Chem. (Liebig), **318**, 183.

atom in isobutyric acid derivatives, X—CO—C$\overset{(CH_3)_2}{\underset{H}{\diagdown\!\!\diagup}}$, is capable of direct alkylation by diphenylmethylene, as is shown by the following experiments :

Alkylation of Benzhydrol Formate.—Benzhydrol formate is readily obtained by heating a solution of 20 grams of potassium formate and 50 grams of bromdiphenylmethane, in formic acid, in a sealed tube, at 100°, for about ten hours. The benzhydrol formate was obtained as a neutral, colorless oil, boiling at 159° to 160° under 10 mm. pressure. An intimate mixture of 10 grams of this oil with 12 grams of sodium benzhydrol was heated in a sealed tube for eight hours, at 300° to 310°, and on working up for acids 0.2 gram pure diphenyl acetic acid, melting at 146°, were obtained ; it was recrystallized from water and ligroin and coincided in its properties with those given in the literature.[1] It is quite probable that a much larger yield could be obtained by further work.

Benzhydrol Isobutyrate, $(CH_3)_2CHCOOCH(C_6H_5)_2$.—A mixture of 50 grams bromdiphenylmethane, 30 grams potassium isobutyrate, and 50 grams isobutyric acid was heated under a reversed condenser for one hour at 150° ; on pouring into water, extracting with ether, washing with sodium hydroxide, and drying the ethereal solution with calcium chloride, 58 grams of benzhydrolisobutyrate, boiling at 185° to 187° under 15 mm. pressure, were obtained. The oil soon changed to a colorless solid which melted at 54°, is quite soluble in cold alcohol and ether, and can be crystallized from low-boiling ligroin.

0.1912 gram substance gave 0.5623 gram CO_2 and 0.1239 gram H_2O.

	Calculated for $(CH_3)_2CHCOOCH(C_6H_5)_2$.	Found.
C	80.3	80.2
H	7.1	7.2

Alkylation of Benzhydrolisobutyrate, 1-Dimethyl-2-diphenyl-

[1] Klingemann : Ann. Chem. (Liebig), **275**, 84 ; Zincke : *Ibid.*, **171**, 122 ; Dunlap : Am. Chem. J., **19**, 645.

propionic Acid, $(C_6H_5)_2CHC(CH_3)_2COOH$.—Nef's experiments with sodium isobutyrate and benzophenone at 190° to 220° have already proved that isobutyric acid is capable of alkylation by diphenylmethylene, and the following experiments simply confirm his results :[1]

1. An intimate mixture of 15 grams of benzyl isobutyrate and 25 grams of sodium benzhydrol was heated in a sealed tube, for five hours, at 190° to 220°. The following products were obtained : 0.8 gram of 1-dimethyl-2-diphenylpropionic acid, in plates, from ligroin, melting at 134° ; 22 grams of benzhydrol ; 4 grams of diphenylmethane ; and benzophenone (4 grams of phenylhydrazone).

2. Twenty-two grams benzhydrol isobutyrate and 15 grams of sodium benzhydrol were heated in a sealed tube, for twenty-six hours, at 100°. Three grams of isobutyric acid and 0.3 gram of monoalkylated isobutyric acid were obtained, besides 16 grams of benzhydrol, 3 grams of diphenylmethane, and 10 grams of unchanged benzhydrol isobutyrate.

3. Fifteen grams each of benzhydrol isobutyrate and sodium benzhydrol were heated in a sealed tube for two and one-half hours, at 270° to 275°. There was some pressure on opening the tube. One-tenth gram benzoic acid and 2.7 grams of 1-dimethyl-2-diphenylpropionic acid (separated by distillation with steam) were obtained. The neutral products were 6 grams of benzhydrol, 4.7 grams of diphenylmethane, and benzophenone (2.4 grams phenylhydrazone).

4. Ten grams of benzhydrol isobutyrate and 20 grams of sodium benzhydrol were heated in a sealed tube, for twenty hours, at 200° to 220°. Only 0.8 gram of monoalkylated isobutyric acid was obtained. The other products were 22 grams benzhydrol, 3 grams diphenylmethane, and benzophenone (5.9 grams phenylhydrazone).

5. Ten grams of benzhydrol isobutyrate and 15 grams sodium benzhydrol were heated in a sealed tube, for eight hours, at 300° to 310°. Four grams of benzoic acid and 3.1 grams monoalkylated isobutyric acid were obtained. The

[1] Ann. Chem. (Liebig), **318**, 184.

neutral portion gave 6.1 grams of diphenylmethane, and benzophenone (5.9 grams phenylhydrazone).

6. Ten grams benzhydrol isobutyrate and 20 grams sodium benzhydrol heated in a sealed tube, for eight hours, at 270° to 300°, gave 6.3 grams of benzoic acid and 2.8 grams of 1-dimethyl-2-diphenylpropionic acid, 8.2 grams diphenylmethane, 1.2 grams benzhydrol and benzophenone (3.6 grams phenylhydrazone) were obtained from the neutral portion.

The experiments 1 to 6 show that, at best, the yield of monoalkylated isobutyric acid is about 30 per cent; the sodium benzhydrol, in great part, decomposes, as such, by heating, and therefore about equal molecules of diphenylmethane and benzophenone (or its decomposition-products) are always obtained.

The Dissociation of Benzhydrol Acetate.—Nef's experiments have proved that benzhydrol and its derivatives, such as benzhydrol ether, benzhydrol ethyl ether, benzhydrol acetate, benzoate, etc., all dissociate at 300° into diphenylmethylene.[1] This explains why, with concentrated sulphuric acid, all these compounds, as well as benzilic acid, give the same deep red coloration which is simply due to the formation of polymerized diphenylmethylene particles. Preliminary experiments by Nef with benzhydrol acetate[2] have shown that this substance decomposes at 300°, giving acetic acid, tetraphenylethylene, and ethane. I have studied this reaction more in detail, with larger amounts of material. Twenty-five grams of benzhydrol acetate were heated in a sealed tube, at 300° to 310°, for twenty-four hours, *i. e.*, for three days of eight hours each. No pressure was noticed on opening the tube, but the contents were dark-colored and gave a strong odor of acetic acid.

On adding sodium hydroxide and ether a portion remained insoluble and was filtered off and dissolved in cold benzene. Tetraphenylethane must, therefore, be absent. The benzene extract gave, on addition of alcohol, 10.8 grams of pure tetraphenylethylene, melting at 221°. Not a trace of β-diphenylpropionic acid (monoalkylated acetic acid) could be found in the alkaline solution. The ether extract gave, on

[1] Ann. Chem. (Liebig), **298**, 231–245.

[2] *Loc. cit.*, p. 244.

fractionation under 10 mm. pressure, 4.9 grams of oil boiling at 140° to 170°. This, on treatment with alcoholic phenylhydrazine, yields 2.5 grams of benzophenone phenylhydrazone, melting at 137°, and 2.1 grams of diphenylmethane boiling at 255° to 260°.

The experiment just described shows that 60 per cent of the benzhydrol acetate decomposes as follows:

$$2(C_6H_5)_2CHOCOCH_3 \rightarrowtail (C_6H_5)_2C : C(C_6H_5)_2 + 2CH_3COOH.$$

The formation of tetraphenylethylene may be due to a direc-polymerization of the diphenylmethylene particles as such, or is more probably due to an alkylation of the non-dissociated benzhydrol acetate by the diphenylmethylene,[1]

$$(C_6H_5)_2C< + H—C\begin{matrix}(C_6H_5)_2\\ \diagup\\ \diagdown\\ OCOCH_3\end{matrix} \rightarrowtail (C_6H_5)_2CHC\begin{matrix}(C_6H_5)_2\\ \diagup\!\!\diagup\\ \diagdown\\ OCOCH_3\end{matrix},$$

with subsequent loss of acetic acid from the addition-product thus formed.

A portion of the diphenylmethylene particles probably also act with the acetic acid as follows:

$$(C_6H_5)_2C< + 2H—OCOCH_3 \rightarrowtail (C_6H_5)_2C(OCOCH_3)_2 + 2H +$$
$$(C_6H_5)_2C=O + (CH_3CO)_2O + 2H.$$

The atomic hydrogen thus set free is at once absorbed by more diphenylmethylene to give diphenylmethane. This explains, in an adequate manner, the formation of benzophenone and diphenylmethane in the dissociation experiment with benzhydrol acetate described above.

Nef has repeatedly called attention to the fact that catalytic agents increase, to a very marked extent, the percentage of dissociated particles present at a definite temperature. The following experiment is of interest in this connection: On May 1st, 1903, I placed in the sunlight a sealed tube containing 10 grams of molten benzhydrol acetate. The liquid soon assumed a yellow color with greenish tinge. The tube stood until Oct. 19th, of the same year, and by that time a considera-

[1] Cf. Nef: Ann. Chem. (Liebig), **335**, 261.

ble amount of solid had separated. A strong odor of acetic acid was noticed on opening the tube; 1.7 grams of tetraphenylethylene, melting at 222°, besides acetic acid and 7.5 grams of unchanged benzhydrol acetate were the only reaction-products obtained.

A preliminary experiment with benzhydrol ethyl ether has shown that it decomposes on heating at 300°, in a distilling-flask, without air access, into acetaldehyde, tetraphenylethane, and benzophenone.[1]

Finally, in this connection, I should like to make some remarks on the dissociation of dibenzyl sulphide, which has recently been worked out by Fromm and Achert.[2] These chemists obtained hydrogen sulphide, toluene, stilbene, thionessal (tetraphenylthiophene), and *s*-tetraphenylbutane as decomposition-products. The results are easily understood on the basis of a primary dissociation of benzyl sulphide into hydrogen sulphide and 2 molecules of phenylmethylene. Dibenzyl has also been noticed as a decomposition-product by previous observers, but not by Fromm and Achert. This was probably due to the fact that, in their experiments, the dibenzyl first formed was entirely alkylated by phenylmethylene as follows:

The following experiment, in which *s*-tetraphenylbutane is obtained from benzyl chloride by simply heating it with dry potassium oxalate, is evidence in favor of the view just presented.

An intimate mixture of 20 grams benzyl chloride and 35 grams anhydrous potassium oxalate was heated in an oil-bath, at 160°, for four hours. By treating the mass with water a small amount of solid remained undissolved. On crystallizing this from a mixture of acetone and alcohol, 1.8 grams of

[1] Cf. Goldthwaite: Am. Chem. J., **30**, 447.

[2] Ber. d. chem. Ges., **36**, 534.

s-tetraphenylbutane, melting at 254° to 255°, were obtained in the form of pearly scales.

On the Action of Sodium on the Benzyl Esters of Acetic, Propionic, Butyric, and Isobutyric Acids—A Revision of Conrad and Hodgkinson's Work.—The experiments of Conrad and Hodgkinson on the action of sodium on the benzyl esters of the acids just named[1] whereby, apparently, the α-monobenzylated derivatives of these esters are obtained as the chief reaction-products have already been briefly discussed above. Such an alkylation is entirely in harmony with the data accumulated by Nef and with my own observations on the action of sodium or sodium benzhydrol on benzhydrol acetate and isobutyrate, respectively. The properties ascribed by Conrad and Hodgkinsin to the esters obtained are, however, so unusual that it seemed very doubtful whether the substances actually prepared had the constitutions assigned to them. The esters in question are all mentioned as being capable of only very slight saponification, even after prolonged digestion with alcoholic potassium hydroxide, or by treatment with soda-lime at higher temperatures. The simplest way to test this point was obviously to synthesize benzyl hydrocinnamate, and then to compare it with the main reaction-product obtained by Conrad and Hodgkinson from sodium and benzyl acetate. This was accordingly done, and the synthetic product was found to behave in an entirely different manner toward alcoholic potassium hydroxide.

Synthesis and Properties of Benzyl Hydrocinnamate, $C_6H_5CH_2CH_2COOCH_2C_6H_5$. — Hydrocinnamic acid was converted into the silver salt by neutralization with ammonia and precipitation with aqueous silver nitrate. The salt was purified by crystallization from hot water, well dried and then heated in a sealed tube, for eight hours, at 100°, with the calculated amount of benzyl chloride, diluted with 2 volumes of absolute ether. Benzyl hydrocinnamate was obtained as a colorless oil, boiling at 190° to 195° under 10 mm. pressure.

0.1527 gram substance gave 0.4463 gram CO_2 and 0.0920 gram H_2O.

[1] Ann. Chem. (Liebig), **193**, 298; **201**, 166.

	Calculated for $C_6H_5CH_2CH_2COOCH_2C_6H_5$.	Found.
C	80.0	79.7
H	6.7	6.7

Ten grams of this oil were at once mixed with the theoretical amount of alcoholic potash and allowed to stand for two hours in the cold. Reaction took place at once, on working up the mixture 3.7 grams of benzyl alcohol, boiling at 204° to 208°, and 5 grams of hydrocinnamic acid, crystallized from ligroin and melting at 48°, were obtained. This striking ease of saponification of benzyl hydrocinnamate is not surprising in view of the statement of Erlenmeyer,[1] "the ethyl ester of hydrocinnamic acid is formed with marvelous ease, likewise it turns acid simply by contact with moist air."

Repetition of Conrad and Hodgkinson's Experiment with Sodium and Benzyl Acetate.—As mentioned above, benzyl acetate and sodium react, in absolute ethereal solution, at ordinary temperatures, giving chiefly sodium benzylate and acetate besides small amounts of diacetyl and benzyl acetoacetate (not over 2 per cent).

A mixture of 100 grams benzyl acetate and 7 grams of sodium, cut in pieces about the size of a pea, does not interact in the cold. It was, therefore, heated, under a reversed condenser, in an oil-bath, with a thermometer in the mixture. As soon as the inside temperature reached 125° a reaction was noticed; the oil-bath was at once removed, the reaction proceeded with violence and the temperature rose to 185°. It is essential for success that there be a great rise of temperature, as previous experiments have proved that, when smaller amounts of material are used and when care is taken to have the reaction proceed more slowly, practically no high boiling products at all are obtained. Even in the experiment just described my yield of high-boiling material was smaller, comparatively, than that given by Conrad and Hodgkinson. The reaction was completed in twenty minutes, and the dark-brown mixture in the flask was treated with dilute sulphuric acid and extracted with ether. The ether extract was then successively

[1] Ann. Chem. (Liebig), **137**, 330.

extracted with sodium carbonate and sodium hydroxide and thus resolved into acid and neutral products. One and one-tenth grams of cinnamic acid, melting at 131°, were found in the carbonate solution. The caustic alkali gave a small amount of oil having the properties of benzyl acetoacetate. The main reaction-products were found to be neutral in character, and were fractionated twice under 10 mm. pressure. A small amount of toluene, boiling at 105° to 108° under ordinary pressure, was obtained from the first fraction ; then came 71 grams of oil boiling from 90° to 100° under 10 mm. pressure. This was obviously what Conrad and Hodgkinson considered to be unchanged benzyl acetate. It consists, however, chiefly of benzyl alcohol. The first fractions, 30 grams, had only the faintest odor of benzyl acetate. The 71 grams of oil obtained gave, furthermore, on treatment with 1.25 mol. alcoholic potassium hydroxide in the cold, 62 grams of pure benzyl alcohol, boiling at 204° to 206°. On further fractionation of the residue in the distilling-flask, 12 grams of oil, boiling at 160° to 190° under 10 mm. pressure, were obtained, and some tar. This oil was now digested for two hours with 3 grams alcoholic potash at 110°, and on working up for neutral and acid products, 3.4 grams of crude hydrocinnamic acid, boiling at 275° to 290°, were obtained. It soon solidified, and gave, on crystallization from ligroin (b. p. 70° to 80°), 3 grams of the pure acid melting at 47°. The neutral portion, distilled twice under 13 mm. pressure, gave 3.2 grams of benzyl alcohol, boiling at 95° to 100°, and 4 grams oil boiling at 155° to 165°. The latter was proved to be benzyl ether by comparison with a synthetic product[1] (b. p. 167° to 168° under 15 mm. pressure), and also by analysis :

0.1922 gram substance gave 0.5962 gram CO_2 and 0.1245 gram H_2O.

	Calculated for $(C_6H_5CH_2)_2O$.	Found.
C	84.8	84.6
H	7.1	7.2

From the above data it is obvious that two-thirds of the high-

[1] Lowe : Ann. Chem. (Liebig), **241**, 374.

boiling oil consisted of benzyl hydrocinnamate and the remaining third of benzyl ether. Judging from their data, Conrad and Hodgkinson must have had relatively far more benzyl ether in their high-boiling oil. It should be emphasized here that benzyl ether burns with great difficulty ; furthermore, that, according to repeated observations of Nef, mixtures of benzyl alcohol and benzyl ether, containing also some phenyl methylene, are very hard to separate completely by fractional distillation under ordinary pressure. Finally, it is clear from the facts presented in this paper that the neutral and high-boiling products obtained by Conrad and Hodgkinson, after treatment with alcoholic potassium hydroxide, must, in all cases, have consisted largely of benzyl ether.

Benzyl Isobutyrate and Sodium Benzylate.—As the action of sodium on benzyl derivatives, in Conrad and Hodgkinson's experiments, obviously depends on the intermediate formation of sodium benzylate, and, owing to the resulting high temperature, on the subsequent alkylation by the phenylmethylene of the products present, the following experiment was carried out in the expectation that a benzylated isobutyric acid would result :

An intimate mixture of 20 grams benzyl isobutyrate and 15 grams sodium benzylate was heated in a sealed tube, for four hours, at 300° to 310°, and then worked up for acid and neutral products : 4 grams of isobutyric acid, 5.8 grams of benzoic acid melting at 122°, but no trace of an α-benzylated isobutyric acid was obtained. The neutral portion contained traces of benzaldehyde, as proved by the isolation of 0.2 gram of phenylhydrazone melting at 156°. The main products were, however, 6.1 grams of benzyl alcohol boiling at 94° to 100° under 10 mm. pressure, and benzyl ether, 8.1 grams, boiling at 130° to 170° under the same pressure. The latter was practically unaffected by digestion with alcoholic potash at 150°. On refractionation, under 8 mm. pressure, 2 grams of oil boiling at 150° to 159°, and 3.5 grams of oil boiling at 159° to 160°, were recovered. Analysis of the latter showed that it was pure benzyl ether.

0.1793 gram substance gave 0.5562 gram CO_2 and 0.1146 gram H_2O.

	Calculated for $(C_6H_5CH_2)_2O$.	Found.
C	84.8	84.6
H	7.1	7.1

According to Lowe (*loc. cit.*), benzyl ether gives toluene and benzaldehyde on prolonged heating at 315°. I have found that pure benzyl ether very slowly yields toluene and benzoic acid on prolonged digestion with alcoholic potassium hydroxide at 150°, or on heating with solid potassium hydroxide or soda-limeat 200°.

It is noteworthy that, in the reaction just described, a large amount of benzyl ether, but not a trace of α-benzylated isobutyric acid is obtained. The corresponding reaction with sodium benzhydrol and benzhydrol isobutyrate, at 300°, gave a 30 per cent yield of monoalkylated isobutyric acid (see above).

Finally, it is to be emphasized here that the substance described by Hodgkinson[1] as α-benzylated isobutyric benzyl ester is exceedingly stable toward alcoholic potash and never gave α-benzylated isobutyric acid by saponification under any conditions. I therefore consider it extremely probable, in view of the data just presented, that Hodgkinson's substance in reality consisted simply of benzyl ether. He succeeded, for instance, in obtaining from it, by means of soda-lime at 200°, toluene and benzoic acid.

In conclusion, I desire to thank Dr. Nef for his painstaking scrutiny and his inspiring interest in connection with this work.

[1] Ann. Chem. (Liebig), **201**, 166.